Mechanical open-loop recycling of post-industrial multilayered PA/PE plastic waste

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ABSTRACT: Plastic packaging generally consists of multiple layers of different polymer materials. These layers are physically connected, for that reason the different polymers can no longer easily be separated from each other. Therefore they must be processed together as a mixture during recycling. This has a negative effect on the properties and processability of these mixtures due to the immiscibility of the polymers, which makes efficient mechanical recycling very challenging. Many of these packaging materials are therefore not yet recycled, but only processed through incineration with energy recovery or end up in landfills. The aim of this research is to examine the effect of different additives on the possibility for open-loop recycling of a post-industrial multilayered waste stream. Therefore, a three layered film consisting of PA and PE, initially used for the sheet moulding compound process, is investigated and is first subjected to an intensive mechanical and rheological characterization. Additionally, the waste is melt-blended with different additives to improve both mechanical and rheological properties as well as the reprocessability. The different upcycled blends are then used to produce injection moulded samples to determine a difference in the properties and processability. Improvements in flow properties were observed by adding both POE and/or talc, which moreover significantly improved the reprocessability into injection moulded test samples. The presence of talc also increased the stiffness of the material, but significantly decreased the elongation at break and impact strength. The same trends, although to a lesser extent, were observed for the mechanical properties when POE was added.

1 INTRODUCTION

Plastic packaging generally consist of a combination of different materials to meet all demanding requirements. Each layer has its one functionality. By combining these layers a structure with enhanced properties can be obtained. Polyamide (PA) for example, is frequently used in multilayered structures because of its excellent barrier properties to gasses, its tear resistance and strength. But the hygroscopic behaviour of PA makes the polymer permeable for moisture. To overcome this infirmity, PA is often combined with a polyolefin. Polyolefins have a good moisture barrier, low cost, great saleability, outstanding toughness and flexibility which is why they are often used in packaging (Morris 2017).

These different layers are physically connected, for that reason the different polymers can no longer easily be separated from each other. Therefore they must be processed together as a mixture during recycling. Usually these polymers are not miscible due to differences in polarity and/or chemical structure. Mechanical recycling will lead to the formation of polymer blends. The immiscibility between the different polymers has a negative effect on the mechanical properties and processability, which makes efficient mechanical recycling very challenging (Ragaert, Delva et al. 2017, Kaiser, Schmid et al. 2018).

To enhance the properties of those mixtures, additives can be used. First of all compatibilizers can be implemented to reduce the immiscibility of the blend. The mechanical properties can be improved by augmenting the adhesion on the interphase between the immiscible components (Ragaert, Delva et al. 2017). Other additives can also be used to augment physical properties like viscosity modifiers, plasticizers, etc. Stabilizers can be employed to prevent or retard degradation reactions. Also mineral fillers (e.g. $CaCO_3$, talc) are often used to optimise mechanical properties or to reduce cost (Castillo, Barbosa et al. 2013).

The main goal of this study is to determine the possibility for open-loop recycling of a post-industrial PA/PE multilayered foil for injection moulding applications. Polymers with a low viscosity are mostly used when extruding foils, therefore open-loop recycling through injection moulding can be a challenge. A polyolefin elastomer (POE) and talc were added in different percentages to improve both rheological and mechanical properties. The possible reprocessability as well as the mechanical and rheological properties of the differed blends are examined.

2 MATERIALS AND METHODS

2.1 *Materials*

The recycled PA/PE foils, delivered by Segers & Balcaen, were initially used as a film barrier for the production of sheet moulding compounds. The film consist of three layers and has a composition of approximately 50/50 vol% (PA-6/LLDPE). Between the different layers there are tie layers present, containing an adhesive. The film waste was already reprocessed by the company and delivered in pellet form.

To improve the flow properties of the recycled material, a PP based elastomer (POE, Vistamaxx 8880) from ExxonMobil was used. It's an ethylene-propylene random copolymer with an ethylene content of 6 wt%. The additive is characterized by a very low viscosity (1200 mPA.s) which enables the material to be used as a viscosity modifier. It also has excellent elastomeric properties, with an elongation at break of around 1237%. The talc, mainly used as a reinforcement, is a PP masterbatch consisting of 74,48 wt% talc from Polyblend.

2.2 *Sample preparation*

For this research, different percentages of the POE and talc were added to the PA/PE matrix. The different compositions are listed in Table 1.

Table 1. Composition of the different blends.

Name	PA/PE [wt%]	POE [wt%]	Talc MB [wt%]
rPAPE	100	-	-
2,5% POE	97,5	2,5	-
5% POE	95	5	-
10% Talc	90	-	10
20% Talc	80	-	20
30% Talc	70	-	30
30% Talc & 5% POE	65	5	30

The materials were melt blended using a co-rotating twin screw extruder (Coperion ZSK18). The screw speed was maintained at 400 rpm for the blends with POE and at 350 rpm for the blends with talc (including the blend with talc and POE). The temperature profile remained unchanged for the different blends and was set at 180 – 230 – 230 – 235 – 235 – 240 – 240 – 250 – 250 °C. Finally, test specimens were produced through injection moulding using an Engel 28T for further characterization of the blends. The temperature profile was set at 200 – 210 – 220 – 230 °C. All test samples were then left to age (23°C and 50% RH) for 48h prior to testing.

2.3 *Characterization*

For an indication of the rheological properties, the melt flow index was measured according to ISO 1133 at a temperature of 230°C and a load of 5 kg.

Tensile properties were obtained using an Instron 5565 dynamometer, according to ISO 527. The initial strain rate was held at 1mm/min. For better accuracy, an extensometer (Instron series 2630 – 100 series) with a gauche length of 50 mm was attached. At a strain level of 0,30%, before the extensometer removal point was reached, the strain rate was increased to 50 mm/min.

For the Charpy impact tests a Tinius Olson IT503 impact tester was used with a nominal impact energy of 7,15 J. The samples were notched 2 mm and tested according to ISO 179. All mechanical tests were carried out at room temperature (23 ± 1 °C) and a relative humidity of 50 ± 5%.

Scanning electron microscopy (SEM) was used to study the surface morphology of the samples using a Phenom G1 SEM. Therefore, injection moulded teste samples were cryogenically broken to examine the brittle fracture surfaces of the samples.

The thermal conductivity of the different talc blends was measured using a Hot Disk TPS 2500 S and 5465 Kapton sensor. Therefore, injection moulded test samples were used. The thermal conductivity was calculated in both radial and axial direction.

3 RESULTS

3.1 *Melt Flow Index and reprocessability*

Figure 1 shows the melt flow index of the different blends. Adding 2,5 and 5 wt% of the POE increases the MFI. The results also show an increasing trend with an increasing amount. By adding only 2,5 wt%, the MFI value is already doubled. This clear increase is due to the very low viscosity of the POE.

Figure 1 also shows an improvement in MFI for the blends containing talc. Adding talc can increase the MFI of the material thanks to its behaviour as a solid lubricant (Ammar, Bouaziz et al. 2017). Talc platelets have the ability to slide against each other during the application of shear forces because of the platy nature which allows an increase in the plastic flow. However, this effect only applies near the die walls, so the effect on the MFI will be minimal (Leong, Bakar et al. 2004). The high increase of the MFI will mostly be attributed to the presence of the PP carrier in the talc masterbatch.

When combining both talc and POE there is no synergetic effect observed. The combinational blend shows a MFI value similar to the blend with only 5 wt% POE.

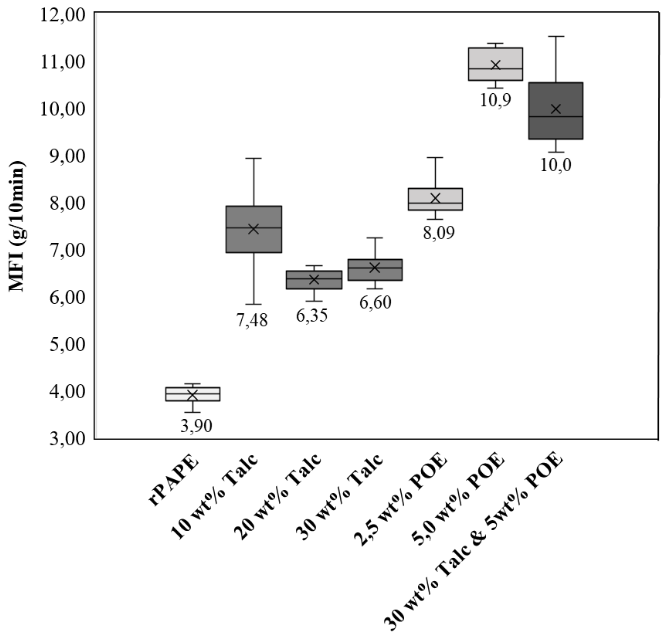

Figure 1. MFI values of the rPAPE matrix and the different blends.

For both additives, the increase in MFI indicates a reduction of the blends viscosity. This has a positive influence on the material flow during reprocessing through injection moulding. In general, a lower holding pressure is needed in function of the amount of additive compared to the parameter used to reprocess the recycled PA/PE.

The blends with 30 wt% talc also results in a reduction of holding pressure, but in addition a significant reduction in holding time is seen. This reduction gives a great advantage for production on a large scale. A lower holding time can be the result of a faster solidification of the sprue which may be caused by a higher thermal conductivity of the talc blends. Figure 2 shows the thermal conductivity of the different talc blends. An improved thermal conductivity can be seen, both in the radial and axial direction, which will certainly help for a faster solidification of the material, however, these results do not give an explanation to the sudden decrease of the holding time needed. To understand this reduction in holding time better, further research with flow simulation software is needed.

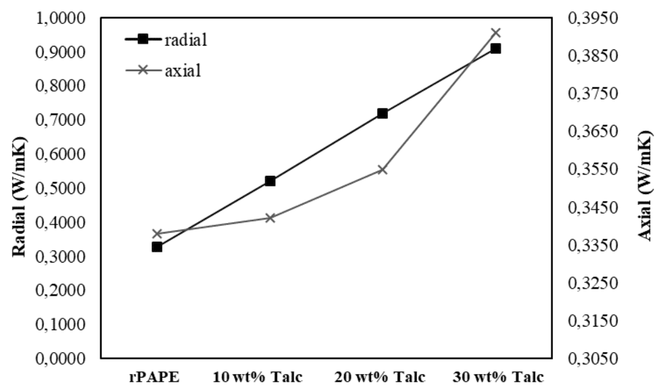

Figure 2. Thermal conductivity of the rPAPE matrix and the different talc blends.

3.2 *Mechanical properties*

3.2.1 *Talc*

The tensile and impact properties of the rPA/PE matrix and the different blends are presented in Table 2. A clear increase in Young's modulus can be observed in the blends containing talc. By adding only 10 wt%, the Young's modulus increased from 678 ± 50 MPa to 1140 ± 39 MPa. The increase in stiffness also results in a slightly higher yield strength. The higher Young's modulus can be due to the reinforcing effect of talc as a filler, but also the orientation of talc can have an influence on the stiffness. A higher reinforcing effect can be achieved when talc is oriented in the direction of the polymer flow (Leong, Bakar et al. 2004). SEM-analyses of the 20 wt% talc blend (Figure 3) show the orientation of the talc plates at different positions in an injection moulded test sample. In the middle of the specimen a core layer is formed in which the talc does not have a preferential orientation. But at the edges, a more broad shear layer can be found where the talc platelets are oriented in the direction of the flow during production.

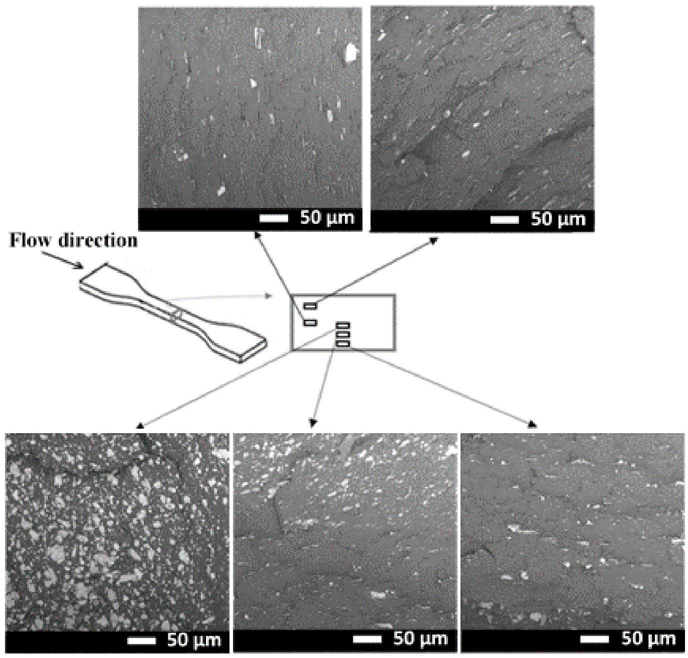

Figure 3: SEM-micrographs (x500) of the PA/PE blend containing 20 wt% talc at different positions of the injection moulded test sample.

As opposed to the improvements in stiffness, the tensile strength, the stress at break and the elongation at break are negatively influenced. The reduction in elongation at break can be attributed to the presence of talc, which suppresses the ability of the matrix to undergo a plastic deformation process (Bakar, Leong et al. 2007). Talc particles can also induce cavitation mechanisms by matrix/filler

Table 2. Mechanical properties of the different materials

	Young's modulus (MPa)	Yield strength (0,2% offset) (MPa)	Tensile strength (MPa)	Stress at break (MPa)	Elongation at break (%)	Impact strength (kJ/m²)
rPAPE	678 ± 50	13,3 ± 0,5	27,7 ± 0,8	27,7 ± 0,8	299 ± 16	93,7 ± 6,4
10 wt% Talc	1140 ± 39	17,0 ± 0,7	25,2 ± 0,2	23,0 ± 0,6	31 ± 3	12,4 ± 2,4
20 wt% Talc	1377 ± 37	17,4 ± 0,4	25,9 ± 0,3	23,6 ± 0,9	18 ± 2	9,8 ± 0,4
30 wt% Talc	1703 ± 97	17,6 ± 0,5	25,9 ± 0,2	22,3 ± 6,7	8 ± 3	7,5 ± 0,1
5 wt% POE	818 ± 37	17,7 ± 0,6	24,4 ± 0,2	21,5 ± 0,3	38 ± 4	20,5 ± 8,4
30 wt% Talc & 5 wt% POE	1332 ± 90	15,2 ± 0,9	22,3 ± 1,3	21,9 ± 1,3	6 ± 1	6,9 ± 0,2

deboning, reducing the elongation at break even further (Wang, Bahlouli et al. 2013). Talc can also act as a stress concentrator, embrittling the matrix (Ammar, Bouaziz et al. 2017). These stress concentration will occur at high loading percentages, where two talc platelets touch and/or at the end of each platelet. Increasing the amount of talc, will increase the amount of stress concentrators resulting in an even more brittle material. These stress concentrations, which will initiate cracks, are also responsible for the reduction in impact strength of the blends (Sánchez-Soto, Rossa et al. 2008). The impact is reduced from 93,7 ± 6,4 kJ/m² to 7,5 ± 0,1 kJ/m² with a talc loading of 30 wt%, nevertheless the resulting impact value is still sufficient for various applications.

3.2.2 *POE*

Table 2 shows a small increase in stiffness in addition of 5 wt% POE but the opposite effect is seen on the tensile and break strength. To prevent a loss in strength, a good adhesion is needed, so the forces applied on the matrix can be transferred to the additive. Nevertheless the results suggest a possible lack of adhesion between both phases, causing a reduction in tensile and break strength (Borggreve, Gaymans et al. 1989).

As mentioned before, the POE is a PP based elastomer. It is a semi-crystalline material with a high amorphous fraction, this allows the material to undergo a large plastic deformation (elongation at break of around 1237%). An increase in elongation at break is therefore expected. However, Table 2 shows a decrease in elongation at break when adding 5 wt% of POE. The same trend is observed when looking at the impact strength which is reduced from 93,7 ± 6,4 kJ/m² to 20,5 ± 8,4 kJ/m² .

It is clear from the reduction in elongation at break and impact strength that the PP based elastomer will disturb the strong PA/PE system resulting in a more brittle material.

Combining both talc and POE significantly reduces the mechanical properties due to the complexity of the resulting blend. Only an improved stiffness is induced as a result of the reinforcing effect of talc.

4 CONCLUSION

This study investigated the possibility for open-loop recycling of post-industrial PA/PE multilayered foils for injection moulding applications by melt blending different percentages of POE and/or talc. Both rheological and mechanical properties as well as the reprocessability were examined.

Adding different weight percentages of POE to the rPA/PE matrix showed a clear increase in MFI. There was also an increasing trend observed when the amount of POE increased. Adding talc had a similar effect, yet to a lesser extent. But no synergetic effect was observed when combining 30 wt% talc with 5 wt% POE. However, both additives have a positive influence on the material flow during reprocessing causing a lower holding pressure needed during injection moulding.

The influence on the mechanical properties were also determined. Adding talc improved the stiffness and yield strength significantly due to a reinforcing effect. But, elongation at break and impact strength were reduced resulting in a more brittle material. The same trends were seen for the blend containing 5 wt% POE. The reduction in elongation at break and impact strength suggest a possible lack of adhesion between both phases. Nevertheless, the resulting impact strength is still sufficient for various applications.

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